INFLUENCE OF BIODIESEL BLENDING ON PHYSICAL AND CHEMICAL PROPERTIES AND EMPIRICAL EQUATION FOR PREDICTING THE PROPERTIES OF BIODIESEL BLEND

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DECLARATION

I declare that this project report entitled "Influence of Biodiesel Blending on Physical and Chemical Properties and Empirical Equations for Predicting The Properties of Biodiesel Blend" is the result of my own work except as cited in the references.

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DEDICATION

Specially dedicated to beloved family, superb lecturers and awesome friends.

"Then which of the favors of your Lord will ye deny?" - (Quran : 55)

ABSTRACT

Biodiesel or also known as fatty acid methyl ester (FAME) is produced from transesterification process which can be obtained from edible or non-edible oil. Instead of using diesel or crude oil only, some modification to the biodiesel has been made as an alternative method of finding renewable energy and reduced cost for the implementation to engine. Blending palm oil biodiesel with diesel able to increase the performance of the reaction of each physical and chemical properties of the blended biodiesel. The important properties of it is shown in the form of empirical equation which is by using second order polynomial curve fitting method. ASTM D6751 is used as the main reference in conducting the experiment of identifying the kinematic viscosity, density, flash point, pour point, cloud point and acid value. The fuel properties of biodiesel blend is close to diesel properties. The kinematic viscosity, density, flash point and acid value is increased proportionally with blending ratio. Cloud point and pour point is also increase but not proportionally as the other parameter regarding to chemical constituent in the blended biodiesel itself. It is also give effect to the value of \mathbb{R}^2 , which is slightly deviate from the value of one.

i

ABSTRAK

Biodiesel atau juga dikenali sebagai Asid Lemak Metil Ester (FAME) terhasil daripada proses transesterifikasi yang mana boleh didapati daripada minyak yang boleh dimakan atau tidak boleh dimakan. Dengan penggunaan diesel atau minyak mentah sahaja, beberapa pengubahsuaian untuk biodiesel itu dibuat sebagai kaedah alternatif untuk mencari tenaga boleh diperbaharui dan pengurangan kos bagi pelaksanaan kepada enjin. Menggabungkan biodiesel minyak sawit dengan diesel komersil dapat meningkatkan prestasi reaksi setiap sifat-sifat fizikal dan kimia biodiesel adun. Ciri-ciri penting ia ditunjukkan dalam bentuk persamaan empirik yang mana dengan menggunakan kaedah pemuat lengkung polinomial peringkat kedua. ASTM D6751 digunakan sebagai rujukan utama dalam menjalankan eksperimen untuk mengenal pasti kelikatan kinematik, ketumpatan, takat kilat, takat curah, takat awan dan nilai asid. Sifat-sifat bahan api biodiesel adun adalah berhampiran dengan sifat diesel. Kelikatan kinematik, ketumpatan, takat kilat tetapi tidak berkadaran dengan nisbah adun. Takat awan dan takat curah juga meningkat tetapi tidak berkadaran seperti parameter lain yang merujuk kepada juzuk kimia biodiesel adun tersendiri. Ia juga memberi kesan kepada nilai R², yang sedikit menyimpang dari nilai satu.

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TABLE OF CONTENTS

| DE | CLARA | TION | |
|-----|---------|---|------|
| DE | DICATI | ON | |
| AB | STRAC | Г | i |
| AB | STRAK | | ii |
| AC | KNOWI | LEDGEMENTS | iii |
| TA | BLE OF | CONTENTS | iv |
| LIS | T OF T | ABLES | vi |
| LIS | T OF FI | GURES | vii |
| LIS | T OF A | BBREVIATIONS | viii |
| СН | APTER | | |
| 1. | INTI | RODUCTION | 1 |
| | 1.1 | Background of Study | 1 |
| | 1.2 | Problem Statement | 2 |
| | 1.3 | Objectives | 3 |
| | 1.4 | Scope of Project | 3 |
| 2. | LITI | ERATURE REVIEW | 4 |
| | 2.1 | Feedstock for Biodiesel Production | 4 |
| | | 2.1.1 Blending of Non Edible Oil Biodiesel with Diesel | 4 |
| | | 2.1.2 Blending of Edible Oil Biodiesel with Diesel | 5 |
| | 2.2 | Common Blended Biodiesel Ratio | 5 |
| | | 2.2.1 B2 (2% Biodiesel, 98% Diesel) | 5 |
| | | 2.2.2 B5 (5% Biodiesel, 95% Diesel) | 5 |
| | | 2.2.3 B20 (20% Biodiesel, 80% Diesel) | 6 |
| | | 2.2.4 B100 (100% Biodiesel, 0% Diesel) | 6 |
| | 2.3 | American Standard Testing Method (ASTM) | 6 |
| | 2.4 | Physical and Chemical Properties of Palm Oil Biodiesel | |
| | | and Diesel | 8 |
| | 2.5 | Chemical Composition In Biodiesel and Diesel | 8 |
| | 2.6 | Physicochemical Properties of Biodiesel Diesel Blending | |
| | | According to ASTM | 10 |
| | | 2.6.1 Kinematic Viscosity | 10 |
| | | 2.6.2 Density | 12 |
| | | 2.6.3 Flash Point | 14 |
| | | 2.6.4 Pour Point and Cloud Point | 15 |
| | | 2.6.5 Acidity Test and Determination of Acid Number | 16 |
| | | 2.6.6 Stability Test | 19 |

| | 2.7 | Empirical Equation | 20 |
|-----|-------|---|----|
| | 2.8 | Use of Blended Biodiesel in Engine | 22 |
| 3. | MET | THODOLOGY | 23 |
| | 3.1 | Flow of Project | 23 |
| | 3.2 | Materials | 25 |
| | 3.3 | Sample Preparation | 25 |
| | 3.4 | Test Method | 27 |
| | | 3.4.1 Stability Test | 27 |
| | | 3.4.2 Density Test | 27 |
| | | 3.4.3 Kinematic Viscosity Test | 28 |
| | | 3.4.4 Acid Number Test | 29 |
| | | 3.4.5 Flash Point Test | 30 |
| | | 3.4.6 Cloud Point Test | 32 |
| | | 3.4.7 Pour Point Test | 32 |
| | 3.5 | Analysis on Physicochemical Properties of Samples | 32 |
| | 3.6 | Empirical Equation | 32 |
| 4. | RES | ULT AND DISCUSSION | 33 |
| | 4.1 | Introduction | 33 |
| | 4.2 | Stability Test | 33 |
| | 4.3 | Density Test | 34 |
| | 4.4 | Kinematic Viscosity Test | 36 |
| | 4.5 | Acid Number Test | 39 |
| | 4.6 | Flash Point Test | 41 |
| | 4.7 | Cloud Point Test | 43 |
| | 4.8 | Pour Point Test | 45 |
| 5. | CON | ICLUSION AND RECOMMENDATIONS | 48 |
| | 5.1 | Conclusion | 48 |
| | 5.2 | Recommendation | 49 |
| REF | FEREN | CES | 50 |

٧

LIST OF TABLES

| TABLE | TITLE | PAGE |
|-------|---|------|
| 2.1 | U.S (ASTM D6751-08) Specification for Biodiesel | 7 |
| 2.2 | Characterization of B0 and B100 | 9 |
| 2.3 | Characterization of Diesel/Biodiesel Blend | 9 |
| 2.4 | Properties of Biodiesel-Blends-Karanja | 11 |
| 2.5 | Physical and Chemical Properties of B100 and B50 | 12 |
| 2.6 | Results for Kinematic Viscosity, Specific Gravity, Calculated Cetane Index and Flash Point Temperature of the Blended Biodiesel Samples | 13 |
| 2.7 | Properties of Standard Diesel (STD), B80, B90 and B100 | 16 |
| 2.8 | Mathematical Relations between Blends Ration and Physico- Chemical Properties | 21 |
| 3.1 | Sample of Biodiesel and Its Blending Ratio | 25 |
| 3.2 | Parameter and Test Method Respectively | 27 |
| 4.1 | Result obtained from stability test | 34 |
| 4.2 | Result obtained from density test | 35 |
| 4.3 | Results obtained from kinematic viscosity test at 40°C | 37 |
| 4.4 | Results obtained from acidity test | 39 |
| 4.5 | Results obtained from flash point test | 41 |
| 4.6 | Results obtained from cloud point test | 43 |
| 4.7 | Results obtained from pour point test | 45 |

LIST OF FIGURES

| FIGURE | TITLE | PAGE |
|--------|---|------|
| 2.1 | Flash Point Graph | 14 |
| 2.2 | Flash Point of Different Blends of Castor Biodiesel and Diesel Fuel | 15 |
| 2.3 | Acid Value of Biofuels, Mineral Diesel and SVO | 19 |
| 3.1 | Flow Chart of Project | 24 |
| 3.2 | Electric Magnetic Stirrer with Thermometer | 26 |
| 3.3 | Sample of Blended Biodiesel | 26 |
| 3.4 | Graduated Scale Hydrometer at 15°C | 28 |
| 3.5 | The 52DV Digital Viscometer | 29 |
| 3.6 | Setaflash Series 3 Plus Closed Cup Flash Point Tester | 31 |
| 4.1 | Density vs. POME Blending Ratio | 35 |
| 4.2 | Kinematic Viscosity vs. POME Blending Ratio | 38 |
| 4.3 | Acid Number vs. POME Blending Ratio | 40 |
| 4.4 | Flash Point vs. POME Blending Ratio | 42 |
| 4.5 | Cloud Point vs. POME Blending Ratio | 44 |
| 4.6 | Pour Point vs. POME Blending Ratio | 46 |

LIST OF ABBREVIATIONS

| ASTM | - | American Society for Testing and Materials |
|-----------------|---|---|
| SVO | - | Straight Vegetable Oil |
| POME | - | Palm Oil Methyl Ester |
| С | - | Carbon |
| Н | - | Hydrogen |
| 0 | - | Oxygen |
| AGO | - | Automotive Gas Oil |
| SFB10 | - | Sterculia Foetida (10% Biodiesel, 90% Diesel) |
| SFB20 | - | Sterculia Foetida (20% Biodiesel, 80% Diesel) |
| RPME | - | Refine Palm Methyl Ester |
| CMB | - | Cerbera Manghas Blending |
| RPMEB | - | Refine Palm Methyl Ester Blending |
| AN | - | Acid Number |
| TAN | - | Total Acid Number |
| NO _X | - | Nitrogen Oxides |
| cSt | - | Centistokes |
| СР | - | Cloud Point |
| РР | - | Pour Point |

CHAPTER 1

INTRODUCTION

1.1 Background of Study

To meet the energy demand and reduce the global warming, biodiesel is able to attract the key attention as an alternative fuel source of renewable energy section which will be replaced of fossil fuel. In the concern of global warming, green fuel can play main rule to reduce greenhouse gas emission. For the future fuel security and reduce greenhouse gases, biodiesel is an automatic choice (Hossain et al. 2013).

Biodiesel is a renewable resource instead of crude oil, which is an infinite resource. It is a methyl ester of fatty acid that made from edible and non-edible oil. It can be blended with diesel at specific percentage. Biodiesel that had been blended will be indicated with a letter 'B' and followed by the blended percentage. Quality of biodiesel can be determined based on physicochemical properties of blended biodiesel. Unblended fuel is referred to B100, which is a pure biodiesel.

Though biodiesel satisfy the ASTM and EN limits, it cannot be used alone in diesel engine due to its high kinematic viscosity and density and also lower oxidation stability and heating value. To improve those properties, it is blended with diesel (Wakil et al. 2015). Some of examples of physicochemical properties is kinematic viscosity, density, calorific value, flash point, cloud point and pour point, cetane number, acid value, heating value, cold filter plugging point and oxidation stability.

1.2 Problem Statement

Due to the environmental problems caused by the use fossil fuels, considerable attention has been made to biodiesel production as an alternative to petrodiesel. Biodiesel is an ecofriendly, alternative diesel fuel prepared from domestic renewable resources, i.e. produced from vegetable oils and animal fats (Alemayehu and Amanu, 2014).

In the U.S., people often say state biodiesel incentives are a backstop to the federal renewable fuel standard (RFS) and, in many cases, they also drive where biodiesel blending infrastructure is installed. Incentives to blend biodiesel vary from usage requirements, such as those in Minnesota and Pennsylvania, to tax breaks and exemptions found in Illinois, Texas and other states. And then there is California's low carbon fuel standard (LCFS), a unique, climate-change-driven standard, mired in court battles, but thought to be the single largest emerging biodiesel market today (Ron, 2013).

Chemical modification to biodiesel by blending it with diesel give less significant changes to other part of component that use the oil especially the engine. Cost can be cut off by using this method. Edible oil that already converts to biodiesel can be used to mix it with diesel. Mixing nature biodiesel with conventional diesel, according to a specific mixing ratio will yield different physicochemical properties to the blended biodiesel.

A polynomial curve fitting method is used to generate a mathematical equation for different biodiesel-diesel blend in order to predict the properties of any percentage of biodiesel in the blend (Wakil et al., 2015)

1.3 Objectives

- i. This study aims firstly at focusing on the physicochemical properties of edible biodiesel and their blends with diesel.
- Empirical equations for various biodiesel blends would be produced in order to predict the important properties of blended biodiesel.

1.4 Scope of Project

- i. Biodiesel is blend with diesel at certain percentage of biodiesel
- ii. Conduct experiment for each physicochemical properties selected based on their own test method
- iii. Produce graph from the result of each test
- iv. Yield empirical equations based on the graph using polynomial curve fitting method
- v. Compare the diesel properties with blended biodiesel

CHAPTER 2

LITERATURE REVIEW

2.1 Feedstock for Biodiesel Production

Biodiesel can be produced from a wide variety of oils which includes vegetable oils (edible and non-edible oils), food processing waste (waste cooking oils), animal fat (tallow, lard, yellow grease, chicken fat), industrial residues, algae, halophytes (Salicomia bigelovii), sewage sludge, etc. Among the available sources of biodiesel, edible oils are dominating in several countries as diesel substitute. For instance, canola and soybean are used in USA, palm oil in Malaysia, rapeseed oil in Europe etc. (Wakil et al. 2015)

2.1.1 Blending of Non Edible Oil Biodiesel with Diesel

According to Mofijur et al. (2015) there have been reported by some author that the potential of biodiesel production from Moringa oleifera, which is a non-edible oil source but there is no extensive report on the characterization of Moringa oleifera biodiesel blend. Study on physical and chemical properties of Moringa oleifera biodiesel and its blends of 10%-90% by volume with diesel had been conducted according to the American Society for Testing and Materials (ASTM D6751) standards and European standards (EN 14214).

2.1.2 Blending of Edible Oil Biodiesel with Diesel

The methyl-ester prepared from soybean oil was blended with diesel fuel such as 10% biodiesel plus 90% diesel, 20% biodiesel plus 80% diesel, 30% biodiesel plus 70% diesel, 40% biodiesel plus 60% diesel, 60% biodiesel plus 40% diesel and 80% biodiesel plus 20% diesel. In the present study, the petroleum analysis of soybean oil, biodiesel (soybean oil methylester) and its different blends with diesel were done and studied. Properties such as fire and flash point, pour point, aniline point, diesel index, specific gravity and cetane number were determined and also distillation characteristics consisting of initial boiling point and final boiling point were also be studied (Goswami and Usmani, 2014)

2.2 Common Blended Biodiesel Ratio

Biodiesel can be legally blended with diesel in any percentage. ASTM International develops specifications for conventional diesel fuel (ASTM D975) (Nair et al. 2013).

2.2.1 B2 (2% Biodiesel, 98% Diesel)

According to Nair et al. (2013), it is one of the most common blends associated with biodiesel. It is used in fleets, tractor trailers, off road heavy equipment, on road light duty fleets.

2.2.2 B5 (5% Biodiesel, 95% Diesel)

Low-level biodiesel blends, such as B5 are ASTM approved for safe operation in any compression-ignition engine designed to be operated on petroleum diesel (Nair et al. 2013).

2.2.3 B20 (20% Biodiesel, 80% Diesel)

Today, B20 is one of the most commonly used form of biodiesel in the USA because it provides a good balance between material compatibility, cold-weather operability, performance, emission benefits, and costs. The B20 blend can be used in most diesel engines with no modifications. Biodiesel blend B20 must meet prescribed quality standards ASTM D7467. Biodiesel contains about 8% less energy per gallon than petroleum diesel. For B20, this could mean a 1% to 2% difference, but most B20 users report no noticeable difference in performance or fuel economy (Nair et al. 2013).

2.2.4 B100 (100% Biodiesel, 0% Diesel)

It has a solvent effect and it can clean a vehicle's fuel system and release deposits accumulated from previous petroleum diesel use. The release of these deposits may initially clog filters and require filter replacement. It may require special handling and equipment modifications. To avoid engine operational problems, B100 must meet the requirements of ASTM D6751. B100 is less common than B5 or B20 due to a lack of regulatory incentives (Nair et al. 2013).

2.3 American Standard Testing Method (ASTM)

Referring to Table 2.1, properties of mixture can be determined by using the standard ASTMD6751-08. For example, flash point can be determined by conducting D93 test method. Other than that, information on oxidation stability can be obtained by ASTM D6751. However, all of the testing method have their own limit. In example, the limit for obtaining cetane number by ASTM D6751 are 47 minute while the limit of determining the acid value by ASTM D664 is 0.5. According to Moser (2009), the ASTM D7467 will be used for B6 – B20. So, it proved that ratio of biodiesel is influencing the testing method and

ASTM table that will be use.

| Property | U.S (ASTN | 1 D6751-08) |
|--|--------------|-----------------|
| | Test Methods | Limit |
| Kinematic viscosity at 40°C (mm ² /s) | D445 | 1.9 - 6.0 |
| Density at 15°C (kg/m ³) | D1298 | 880 |
| Calorific value (MJ/kg) | - | - |
| Flash point (°C) | D3278 | 93 min. |
| Pour point (°C) | D97 | -15 to 16 |
| Cloud point (°C) | D2500 | -3 to 12 |
| Cloud filter plugging point (CFPP) (°C) | D6371 | Max +5 |
| Cetane number | D613 | 47 min. |
| Oxidation stability at 110°C (h) | D675 | 3 min. |
| Acid value (mgKOH/g) | D664/D974 | 0.5 max. |
| Free glycerin (wt% max) | D6584 | 0.02 |
| Total glycerin (wt% max) | D6584 | 0.24 |
| Carbon residue (wt% max) | D4530 | 0.05 |
| Copper strip corrosion (3 h at 50°C) | D130 | No. 3 max. |
| Iodine value (g/l ₂ /100 g) max | - | - |
| Water and sediments (vol%, max) | D2709 | 0.05 |
| Total sulphur (ppm), max | D5453 | 15 ^b |
| Phosphorus (ppm), max | D4951 | 10 |

Table 2.1: U.S (ASTM D6751-08) Specification for Biodiesel

(Source: Wakil et al. 2015)

2.4 Physical and Chemical Properties of Palm Oil Biodiesel and Diesel

Transesterification reaction reduces the calorific value, density, cloud point sulphur content and carbon residue of palm biodiesel. Palm biodiesel has a lower calorific value, however, the higher cetane level compensates for this advantage, in example, palm biodiesel has higher quality combustion, making better use of its energy content. In addition, distillation of palm biodiesel indicates that the fuel is volatile with the dynamic viscosity, increasing with the palm oil content. However, the tendency of palm biodiesel to form carbon during combustion is observed to be less compared to diesel. Other than that, biodiesel is more lubricating than diesel (Nagi et al., 2008).

2.5 Chemical Composition in Biodiesel and Diesel

According to Benjumea et al. (2008), biodiesel contain mixture of mono-alkyl ester of saturated and unsaturated long chain fatty acids. While, diesel contain mixture of paraffinic, naphthenic and aromatic hydrocarbon. Each molecule of fatty acid containing a carboxyl group which is carbon, hydrogen and oxygen that are attached to carbon atom chain with its respective hydrogen atom. As for diesel, aromatic hydrocarbon is an oxidation resistant and higher saturation reduces the oxidation problem. Different properties between the two types of fuel giving out different result from experiment. Mixing the diesel with palm oil biodiesel (POME) is giving out new physical and chemical characteristic of fuel. Physical characteristics are including the pour point, flash point, cloud point, viscosity boiling point, etc. While chemical characteristics are the acid value, saponification value, etc. As the blending ratio is increasing from B0 to B100, the percentage of carbon and hydrogen will decreased. While the percentage of oxygen is increased. Table 2.2 and 2.3 showing the chemical composition contain biodiesel and its blend.

| Diesel/Biodiesel | Molecular | С, % | Н, % | 0,% | Density, | Surrogate |
|------------------|-----------|-------|-------|-------|----------|---|
| blends | weight, | | | | kg/l | |
| | g/mol | | | | | |
| B0 | 191.8 | 86.93 | 12.96 | 0.07 | 0.8369 | C _{13.89} H _{24.86} O _{0.01} |
| B100 | 295.31 | 76.96 | 12.17 | 10.83 | 0.8693 | C _{18.94} H _{36.03} O ₂ |

Table 2.2: Characterization of B0 and B100

(Source: Dinh and Hoang, 2014)

Table 2.3: Characterization of Diesel/Biodiesel Blend

| Diesel/Biodiesel | Molecular | C, % | H, % | 0,% | Density, | Surrogate |
|------------------|-----------|-------|-------|------|----------|---|
| Blends | Weight, | | | | kg/l | |
| | g/mol | | | | | |
| B5 | 195.35 | 86.41 | 12.92 | 0.63 | 0.8385 | C _{14.07} H _{25.24} O _{0.08} |
| B10 | 199.02 | 85.90 | 12.88 | 1.18 | 0.8401 | C _{14.25} H _{25.63} O _{0.15} |
| B15 | 202.81 | 85.39 | 12.84 | 1.74 | 0.8418 | C14.43H26.04O0.22 |
| B20 | 206.74 | 84.87 | 12.80 | 2.29 | 0.8434 | C14.62H24.46O0.3 |
| B30 | 215.02 | 83.86 | 12.72 | 3.38 | 0.8466 | C15.03H27.34O0.45 |
| B40 | 223.91 | 82.85 | 12.64 | 4.47 | 0.8499 | C15.46H28.3O0.63 |
| B50 | 233.50 | 81.85 | 12.56 | 5.55 | 0.8531 | C15.93H29.32O0.81 |
| B60 | 243.86 | 80.86 | 12.48 | 6.62 | 0.8563 | C16.43H30.43O1.01 |
| B70 | 255.10 | 79.87 | 12.40 | 7.69 | 0.8596 | C16.98H31.63O1.23 |
| B80 | 267.32 | 78.89 | 12.32 | 8.74 | 0.8628 | C17.58H32.94O1.46 |
| B90 | 280.67 | 77.92 | 12.25 | 9.79 | 0.8661 | C _{18.23} H _{34.37} O _{1.72} |

(Source: Dinh and Hoang, 2014)

According to table above, research made by Dinh and Hoang (2014) said that as the blending ratio is increasing from B0 to B100, the percentage of carbon and hydrogen will decreased. While the percentage of oxygen is increased. Which means that, the longer the carbon chain of fatty acid, the more saturated the molecule. The shorter the carbon chain, the more unsaturated the molecule with the existence of double bond chain.

2.6 Physicochemical Properties of Biodiesel Diesel Blending According to ASTM

Biodiesel is completely miscible with diesel and the blending in any proportion is possible in order to improve the fuel qualities (Silitonga et al. 2013). Accordingly, it has become easier to have a clear concept of the physicochemical properties of edible and nonedible vegetable oils with varying blending percentages for a better understanding on blend qualities (Wakil et al. 2015).

2.6.1 Kinematic Viscosity

Kinematics viscosity of Karanja Biodiesel which is then blended with diesel at mixing ratio of B0, B20, B40, B60, B80 and B100 are studied (Sivaramakrishnan and Ravikumar, 2012). The result from the experiment shows that the value of kinematics viscosity are increasing along with the increasing of biodiesel mixing ratio. The result is tabulated in Table 2.4.

| Biodiesel | Kinematics viscosity (mm ² /s) | Heating value (MJ/kg) | Flash point (°C) | Density (kg/l) | Cetane number |
|-----------|---|-----------------------------|------------------------|-------------------|------------------|
| B0 | 2.71 | 42.5 | 55 | 0.836 | 51.00 |
| B20 | 4.01 | 41.5 | 65 | 0.849 | 51.70 |
| B40 | 5.23 | 39.9 | 77 | 0.858 | 52.82 |
| B60 | 6.72 | 38.7 | 88 | 0.862 | 53.15 |
| B80 | 8.19 | 37.0 | 101 | 0.878 | 53.86 |
| B100 | 9.60 | 35.9 | 114 | 0.900 | 54.53 |

Table 2.4: Properties of Biodiesel-Blends-Karanja

(Source: Sivaramakrishnan and Ravikumar, 2012)

There are condition where, the kinematics viscosity of blended biodiesel is suitable to be use in automobile engines. ASTM Standards (ASTM6751) showed that the kinematic viscosity of B100 is high and cannot be use for engine B50 is within the standards range in spite that its kinematic viscosity is at the upper limit of working conditions. Referring to Table 2.5, the properties of pure jatropha biodiesel (B100) and blended jatropha (B50) were compared with petrodiesel and B20. Kinematic viscosity which is the major problem of jatropha oil applied in biodiesel production is high for both B100 and B50. The kinematic viscosity of B100 is above the working limit of petro diesel. Pure jatropha biodiesel cannot be used for engine without blend with diesel (Abadi and Omer, 2015).

| Physicochemical property | B100 | B50 | B20 | Diesel |
|----------------------------------|-------|-------|-------------|-------------|
| Specific gravity | 0.865 | 0.841 | 0.87 - 0.89 | 0.85 |
| Density 15°C, g/cm ³ | 0.881 | 0.863 | 0.88 | 0.82 - 0.87 |
| Kinematics viscosity (40°C), cSt | 4.51 | 4.04 | 1.9 – 6.0 | 1.3 – 4.1 |
| Flash point (°C) | 172 | 87 | 52 min. | 60 - 80 |
| Cloud point (°C) | 1 | 2 | -3 to 12 | -15 to 5 |
| Carbon residue (10% | 0.3% | 0.1% | 0.35 max. | 15% |
| distillation) | | | | |
| Cetane number | 49.5 | 49.5 | 40 min. | 40 - 55 |

Table 2.5: Physical and Chemical Properties of B100 and B50

(Source: Abadi and Omer, 2015)

2.6.2 Density

From the research of Benjumea et al. (2008) state that, density of palm oil biodieseldiesel fuel blends (B0, B5, B20 and B100) is measured at various temperature which is from 289 to 373 K. The result shows that, there is a linear variation of density relative to the biodiesel content in the mixtures. And also, there was a linear function of temperature for the palm oil biodiesel, diesel and blends. This statement is fully supported by Ramírez-Verduzco et al. (2011) in which experiment is conducted to B0, B1, B5, B10, B15, B20, B60 and B100 at various temperature from 293.15 to 373.15 K. The results shows that, for a given fixed temperature, the density increases approximately 1.0062 times by each 10 vol.% of biodiesel content.

The standard specific gravity values for diesel fuels range between 0.8200 to 0.8700. From the results obtained in Table 2.6, all the four-blended biodiesel samples were within the acceptable range of values. However, it was observed that as the blending ratio increased, the specific gravity values also increased. More biodiesel in the mixture (blend) increased the density of the final blended sample, hence the increase in specific gravity